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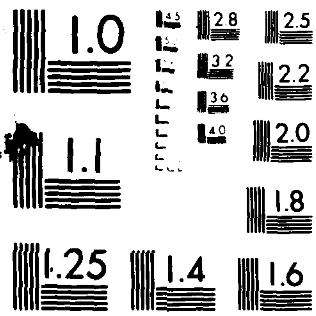

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Renormalization Group Treatment for O/W(110)*

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We consider the lattice gas model of the O/W(110) chemisorption system. We calculate the transition temperature T_c at one half coverage by means of a new renormalization group treatment. Good agreement ($\lesssim 10\%$) with T_c obtained via Monte Carlo studies is found over a wide range of parameter values. We explore the remarkable independence of T_c from ε_1, the nearest neighbor adatom-adatom interaction. We also give several arguments indicating that the transition at this coverage is in the simple Ising universality class.

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1. Introduction

The interaction between adsorbed atoms is a fundamental property of adsorption systems. The understanding of many important surface phenomena such as corrosion, oxidation, hetergeneous catalysis and crystal growth will be enhanced by a knowledge of these forces. In order to fully understand adatom-adatom interactions it is necessary to start with a study of adatom behavior in submonolayer systems. This allows the isolation of the effect from the many other phenomena occuring in adsorption systems.

Much progress has been made in the ab initio calculation of adatom-adatom (AA) interactions, especially for physisorbed layers. Here we consider the strong chemisorption system O/W(110). In this kind of system indirect AA interactions, mediated by the substrate conduction electrons, are important. A general theory of these forces exists[1] but in order to determine AA couplings for any specific case it is necessary to proceed by a more indirect route. In the O/W(110) system models for the AA interactions have been derived by making use of statistical mechanics.[2,3] In the submonolayer regime, for T $\gtrsim$ 300°K, the O overlayer is in thermodynamic equilibrium.[4] Hence its thermodynamic phase is determined by the A-A interactions. The phase diagram of this system can be measured with a combination of LEED (Low Energy Electron Diffraction) and Auger techniques. Using statistical mechanics, one can then compare the experimental phase diagram[5] with one calculated from an assumed set of AA coupling constants. This can be done for various parameter values, and the best AA interaction energies may be determined. This program has been carried out for O/W(110) using the Monte Carlo method.[2,3] This is a very powerful numerical technique, but its repeated use requires non-trivial amounts of computer time. In this work we show that comparable results may be obtained more efficiently with a renormalization group method. This type of calculation was originally applied by Wilson to the problem of determining thermodynamic behavior near critical points. It has more recently

been recognized as also providing a powerful tool for approximating the global free energy and phase behavior.

In this work we apply an existing position space renormalization group (PSRG) technique, the modified Kadanoff variational method (MKVM)[6] to the problem of O/W(110). The model used for this adsorption system is a lattice gas with interactions through 4th nearest neighbor. Thus our work represents a significant extension of existing PSRG methods.[7] For the case of one half coverage we find excellent agreement with previously reported Monte Carlo results over a wide range of parameter values.

In section 2 we introduce the lattice gas model for our adsorption system and describe a certain useful approximation we have developed for it. Section 3 describes the MKVM as applied to this system. In section 4 we present our results and compare them with those obtained by the Monte Carlo method. Section 5 we discuss the critical properties of the model. We point out that there is considerable evidence that the order-disorder transition at one-half coverage is Ising like. In section 6 we mention some problems for future research.

2. Definition of Model and the ϵ_1 Approximation

The adsorption sites for O on the W(110) have the geometry illustrated in Fig. 1. Note that this two-dimensional lattice may be regarded as two interpenetrating rectangular sublattices R and R'.

The Hamiltonian for this system may be written as

$$\mathcal{H} = \epsilon_1 \sum_{\langle nn \rangle} \tau_i \tau_j + \epsilon_2 \sum_{H} \tau_i \tau_j + \epsilon_3 \sum_{V} \tau_i \tau_j + \epsilon_4 \sum_{D} \tau_i \tau_j \tag{1}$$

The occupation number $\tau_i = 1$ (0) for an occupied (empty) adsorption site. The AA energies ϵ_i are defined with respect to the (isolated) single adatom adsorption energy ϵ_o. This is of the order of several eV and plays no role at the temperatures of interest here since $kT \ll \epsilon_o$. $\langle nn \rangle$ denotes a sum over all distinct nearest neighbor adsorption site pairs, H over (horizontal) second neighbor pairs, v over (vertical) third neighbor pairs, and D over fourth

neighbor pairs in the diagonal directions. The grand partition function is

$$\mathcal{G}_G(z,N,T) = \sum_{N_a=0}^{\infty} z^{N_a} \sum_{\{\tau_i\}}{}' e^{-\beta\mathcal{H}(\tau_1\cdots\tau_N)} \tag{2}$$

where $\sum_{\{\tau_i\}}{}'$ represents a sum over all possible occupation numbers satisfying

$$\sum_{i=1}^{N} \tau_i = N_a \tag{3}$$

and removing the prime removes this restriction. N is the number of adsorption sites. Eq (2) may be rewritten using spin variables

$$\mathcal{G}_G(z,N,T) = \sum_{\{\sigma_i\}} e^{H(\sigma_1\cdots\sigma_N)} \tag{4}$$

where

$$\begin{aligned} H = & -[\ln z/2 + (\beta/4)(2\epsilon_1+\epsilon_2+\epsilon_3+2\epsilon_4)] \\ & -[\ln z/2 + (\beta/4)(4\epsilon_1+2\epsilon_2+2\epsilon_3+4\epsilon_4)]\sum\sigma_i \\ & -(\beta\epsilon_1/4)\sum_{\langle nn\rangle}\sigma_i\sigma_j - (\beta\epsilon_2/4)\sum_{H}\sigma_i\sigma_j - (\beta\epsilon_3/4)\sum_{V}\sigma_i\sigma_j - (\beta\epsilon_4/4)\sum_{D}\sigma_i\sigma_j \end{aligned} \tag{5}$$

Here $\sigma_i = 2\tau_i - 1$ so $\sigma_i = +1$ (spin up) corresponds to $\tau_i = +1$ (filled) site and $\sigma_i = -1$ (spin down) to $\tau_i = 0$ (empty site). Now Eq(5) is an even function of σ_i when

$$\ln z/2 + (\beta/4)(2\epsilon_1+\epsilon_2+\epsilon_3+2\epsilon_4) = 0 \tag{6}$$

Hence imposing Eq(6) implies that the coverage $\theta = \bar{N}a/N = 1/2$.

Now as pointed out above, the adsorption sites for O/W(110) may be regarded as two interpenetrating sublattices R and R', as shown in Fig. 1. Hence Eq(5) may be written as

$$H = -\sum_{R} V_R(\sigma_R) - \sum_{R'} V_2(\sigma_{R'}) - (\beta\epsilon_1/4)\sum_{\langle nn\rangle}\sigma_i\sigma_j \tag{7}$$

where

$$\begin{aligned} V_R(\sigma_R) = & (\beta/4)(2\epsilon_1+\epsilon_2+\epsilon_3+2\epsilon_4) + (\beta\epsilon_2/8)(\sigma_1\sigma_2+\sigma_3\sigma_4) \\ & + (\beta\epsilon_3/8)(\sigma_2\sigma_3+\sigma_1\sigma_4) + (\beta\epsilon_4/4)(\sigma_1\sigma_3+\sigma_2\sigma_4) \end{aligned} \tag{8}$$

and $\sigma_1, \sigma_2, \sigma_3, \sigma_4$ are spin variables for one cell in the rectangular lattice

R as shown in Fig. 2. The sums on R and R' in Eq(7) are over distinct 4-spin sublattice cells.

Note that ϵ_1 is the only A-A interaction term coupling sublattices R and R' in Eq(7). Even though this energy is as large or larger than the further neighbor coupling terms, it turns out to have very little effect on the value of the (order-disorder) transition temperature $T_c^{\frac{1}{2}}$ at coverage $\theta = \frac{1}{2}$. This was already noted, for a certain range of ϵ_1 values, by Williams et al[2] in their Monte Carlo study of this model. We examine this ϵ_1 indepence further and use it in our PSRG treatment below.

Now for O/W(110) the ordered (low-temperature) state at $\theta = \frac{1}{2}$ is (2x1). This ordering also occurs at low coverages (although the transition temperature drops abruptly for $\theta \lesssim 0.3$).[5] These facts imply that one may take

$$\begin{aligned} \epsilon_1, \epsilon_4 &< 0 \\ \epsilon_2, \epsilon_3 &> 0 \end{aligned} \tag{9}$$

(In fact one could also let ϵ_2 and ϵ_3 be slightly negative).

Consider a perfectly ordered (2x1) state at $\theta = \frac{1}{2}$. Moving an adatom to the most favorable disordered site raises its energy by $2\epsilon_2 + \epsilon_3 - \epsilon_4$ or $2\epsilon_3 + \epsilon_2 - \epsilon_4$, a quantity independent of ϵ_1. This implies that $T_c^{\frac{1}{2}}$ depends on ϵ_1 weakly at best, as is verified in Ref. 2 for large values of ϵ_1.

When ϵ_1 is small we may also use an argument following Kadanoff and Wegner.[8] Eq(9) implies that the sublattices R and R' will be antiferromagnetically ordered at low temperatures. Hence the Hamiltonian is of the form of two interpenetrating antiferromagnetic square lattices coupled ferromagnetically

$$-\beta H' = k \sum_{\langle nn \rangle} \sigma_i \sigma_j + k \sum_{\langle nn \rangle} \sigma_i' \sigma_j' - K_1 \sum_{\langle nnn \rangle} \sigma_i \sigma_j' \tag{10}$$

where k, $k_1 > 0$. In Eq(10), σ_i are spins on sublattice R, σ_i' on sublattice R', and the three sums are over nearest neighbor pairs both on R, both on R' and one on each, respectively. Now for $K_1 = 0$ we have two independent lattices with an antiferromagnetic transition at coupling K_c. The correlation function associated with the operator connecting the two lattices is

$$g(r) = \langle \sigma_i \sigma_j' \sigma_{i+r} \sigma_{j+r}' \rangle \tag{11}$$

where i and j are nearest neighbors on R and R'. For $K_1 = 0$, at the critical point one has

$$g_c(r) = \langle \sigma_i \sigma_{i+r} \rangle_{K_c} \langle \sigma_j' \sigma_{j+r}' \rangle_{K_c}$$
$$= \langle \sigma_i \sigma_{i+r} \rangle_{K_c}^2 \sim \frac{1}{r^{2x}} \tag{12}$$

To evaluate x, we must examine the large r behavior of the ferromagnetic correlation function at the antiferromagnetic critical point. By up-down spin symmetry, this is the same as the antiferromagnetic (staggered) correlation function at the ferromagnetic critical point. This falls off more rapidly with r than the ferromagnetic correlation function, for which $x_F = d + \eta = 9/4$ (in two dimensions). Hence we must have $x > 9/4$. Now let

$$\chi(r, r') \equiv \langle \sigma_r \sigma_{r'} \rangle_c \tag{13}$$

Then the antiferromagnetic correlation function may be written approximately as

$$g_{AF}(r) = \frac{1}{4} \langle (\sigma_0 - \sigma_a)(\sigma_r - \sigma_{r+a}) \rangle \tag{14}$$

where a is a lattice spacing. For $r \to \infty$ this reduces to

$$g_{AF}(r) \sim \frac{d^2}{dr^2} g(r) \sim \frac{1}{r^{17/4}} \tag{15}$$

Thus $x = 17/4$. Now $y = d - x = 2 - 17/4 = -2\ 1/4 < 0$. Hence the operator coupling the two lattices (the third term in Eq(7)) is irrelevant at the fixed point. This means that for small K_1 it should have a vanishing affect on the renormalization group flows and hence not affect $T_c^{1/2}$.

Since this argument depends only on the long distance behavior of certain correlation functions and the types of coupling present, it is valid for many Hamiltonians. In particular, Eq(7) for $\epsilon_1=0$ has an Ising type critical point when $\epsilon_3(4)$ holds. Hence $\eta = 1/4$ and the argument remains valid. We use it below to justify treating the ϵ_1 term in Eq(7) approximately.

Actually the weak dependence of $T_c^{1/2}$ on ϵ_1 extends over a wide range of ϵ_1 values. This is illustrated in columns 4 and 5 of Table I where we list T_c for the parameter values in Columns 1, 2 and 3 as determined by Monte

Carlo calculations[2] (Col. 4) and T_c[½] for $\epsilon_1 = 0$ as given by the free fermion approximation of Fan and Wu[9] (col.5). The uncertainty in col. 4 is $\pm 10^{\circ}$K and the col. 5 values are about 3% too large[10] for the parameters shown.

3. Method of Calculation

In this section we describe the MKVM technique[6] and how it is applied to our model for O/W(110). This is defined by Eq(7). First we consider the case of $\epsilon_1 = 0$, so that the two sublattices (see Fig 1 and Section 2) are decoupled. Later we include ϵ_1 via a preliminary transformation.

For $\epsilon_1 = 0$ the remaining terms in Eq(7) are completely independent Eq(4) reduces to

$$\mathcal{Z}_G(z,N,T) = \sum_{\{\sigma_i,\sigma_i'\}} e^{-\sum V_R(\sigma_R) - \sum V_R(\sigma_R')} = \left[\sum_{\{\sigma_i\}} e^{-\sum V_R}\right]^2 \tag{16}$$

Thus the free energy is given by

$$\beta P_G = (2/N) \ln \sum_{\{\sigma_i\}} e^{-\sum_R V_R(\sigma_R)} \tag{17}$$

We calculate βP_G and its derivatives using the modified Kadanoff variational method (MKVM). With the signs of the AA energies ϵ_i defined in Eq(9), an antiferromagnetic coupling is favored on each of the sublattices R and R'. To obtain a viable cell spin definition in the MKVM (especially at low temperatures), we must redefine spin variables so that ferromagnetic ordering is favored. For each cell in sublattice R (and likewise for R') we let $\sigma_1 \to \sigma_1$, $\sigma_2 \to -\sigma_2$, $\sigma_3 \to \sigma_3$, $\sigma_4 \to -\sigma_4$ or $\sigma_1 \to -\sigma_1$, $\sigma_2 \to \sigma_2$, $\sigma_3 \to -\sigma_3$, $\sigma_4 \to \sigma_4$ where $\sigma_1, \sigma_2, \sigma_3, \sigma_4$ are illustrated in Fig. 2. The two different kinds of spin redefinition are performed alternately, so that the configuration sum in Eq(17) is equivalent to a configuration sum in the original variables with $\epsilon_2, \epsilon_3, \epsilon_4$ replaced by $-\epsilon_2, -\epsilon_3$, and ϵ_4 respectively. Then we apply the MKVM to Eq(17) with $\epsilon_2, \epsilon_3, \epsilon_4$ replaced by $-\epsilon_2, -\epsilon_3, \epsilon_4$. Thus V_R becomes

$$V_R(\sigma_R) = \beta/4)(2\epsilon_1 - \epsilon_2 - \epsilon_3 + 2\epsilon_4)$$

$$- (\beta/8)\epsilon_2(\sigma_1\sigma_2 + \sigma_3\sigma_4) - (\beta/8)\epsilon_3(\sigma_2\sigma_3 + \sigma_4\sigma_1) + (\beta/4)\epsilon_4(\sigma_1\sigma_3 + \sigma_2\sigma_4) \quad (18)$$

(Note also that this transformation changes the term coupling to $\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$ into a "staggered field" term. The coefficient of this term vanishes for $\Theta = \frac{1}{2}$, however.)

Now we review the MKVM technique.[6] The transformed cell potential V' for the new lattice with doubled lattice spacing is related to the original cell potential V by the RG transformation equation:

$$e^{V'(\mu)} = \sum_{\sigma_1 \cdots \sigma_4} e^{z V(\sigma_1 \cdots \sigma_4) + p \sum_i^4 \mu_i \sigma_i - u(\sigma_1 \cdots \sigma_4)} \quad (19)$$

where

$$u(\sigma_1 \cdots \sigma_4) = \ln 2 \cosh p(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

Z = no. of nearest neighbors = 4, and $\mu = (\mu_1, \mu_2, \mu_3, \mu_4)$ are spin variables in the new lattice with $\mu_i = \pm 1$. The variational parameter p is determined by minimizing the single cell free energy. This leads to the nonlinear equation

$$\frac{\sum_{\mu_1 \cdots \mu_4} \frac{\partial V'}{\partial p} e^{V'(\mu)}}{\sum_{\mu_1 \cdots \mu_4} e^{V'(\mu)}} = 0 \quad (20)$$

which is solved at each iterative step to determine p.

To begin with, we use V of Eq.(18) in the right hand side Eq(19) with p given by Eq(20), and calculate the transformed cell potential V' from Eq(19). This constitutes the first step of the RG transformation. Note that this step in general gives rise to a non-zero four spin coupling term ($\alpha \mu_1 \mu_2 \mu_3 \mu_4$) as well as the terms of Eq(8). In addition there will be an additive constant term in V' (μ). We then use V'(μ) thus obtained as input in the same procedure to calculate the transformed potential V"(μ). This RG transformation is iterated further so that a series of cell potentials V'(μ), V"(μ)

and corresponding variation parameters $p^{(1)}, p^{(2)}......p^{(\alpha)}$, .. are obtained In this step by step RG transformation, the variational parameters $p^{(\alpha)}$ and coupling constants $\beta\epsilon_i^{(\alpha)}$ contained in $V^{(\alpha)}$ (ie the coefficients of the spin dependent terms) tend to diminish to zero when the system is in a disordered state and tends to grow when the system is in an ordered state. For a given initial set of ϵ_2, ϵ_3, ϵ_4, we can therefore adjust β to obtain the order-disorder transition temperature from the behavior of p and the coupling constants after many RG transformations.

After the αth RG transformation, the free energy βPG of Eq(17) may be approximated by

$$\beta P_G = (1/4^{\alpha})\,(\max V^{(\alpha)}(\mu)) \tag{21}$$

when α is sufficiently large. Eq(21) contains the contribution to the free energy from the spin-independent constant terms in each $V^{(i)}$ as well as an approximation for the contribution from the spin-dependent part of $V^{(\alpha)}$. We can also calculate the first and the second derivative of βPG with respect to temperature and thus obtain the internal energy and specific heat of the system. Such calculations involve evaluating the product of a series of matrices $\frac{\partial V'}{\partial V^0}, \frac{\partial V''}{\partial V'}, \cdots \frac{\partial V^{(\alpha)}}{\partial V^{(\alpha-1)}}$ or differentiating numerically and will be detailed in another paper.

In discussing the MKVM we have neglected the coupling between the spins in the R and R' sublattices completely up to now, i.e. we have let $\epsilon_1 = 0$ in the last term in Eq(7). As argued in Section 2, this term is unimportant near T_c. Therefore we may take its effect into account approximately. Eq(11) may be rewritten a

$$H = \Big[-\sum_R V_R(\sigma_R) - \epsilon_1/5)\sum_{\langle nn\rangle}\sigma_i\sigma_j\Big] + \Big[-\sum_{R'} V_R(\sigma_{R'}) - \epsilon_1/5)\sum_{\langle nn\rangle}\sigma_i\sigma_j\Big] \tag{22}$$

The coupling of spins · the fir· bracket is shown in fig. 3. In addition to the interaction energy $V_R(\sigma_R$ n each cell, which has four spins $\sigma_1, \sigma_2, \sigma_3, \sigma_4$

in the corners, there is one additional spin, say σ_5, in the center, which interacts with each corner spins with coupling constant $\epsilon_1/8$. These central spins actually interact with each other via the first term in the second bracket of Eq(22). In our approximation, we neglect this interaction between the spins in the first and the second brackets. We consider the effect of the central spin in the first bracket as being only to produce a certain effective coupling among the corner spins. In this approximation, we still have two decoupled sublattices. We carry out the configuration sum for the central spin first and obtain the effective cell potential for the corner spins:

$$
\begin{aligned}
V_R^{eff}(\sigma_R) = {} & (\beta/4)(2\epsilon_1+\epsilon_2+\epsilon_3+2\epsilon_4) + (\beta\epsilon_2/8)(\sigma_1\sigma_2+\sigma_3\sigma_4) \\
& + (\beta\epsilon_3/8)(\sigma_2\sigma_3+\sigma_4\sigma_1) + (\beta\epsilon_4/4)(\sigma_1\sigma_3+\sigma_2\sigma_4) \\
& + \ln\left(\exp(\beta\epsilon_1/8)(\sigma_1+\sigma_2+\sigma_3+\sigma_4) + \exp(-\beta\epsilon_1/8)(\sigma_1+\sigma_2+\sigma_3+\sigma_4)\right)
\end{aligned}
\tag{23}
$$

We now obtain effective initial values of $\epsilon_2, \epsilon_3, \epsilon_4$, the four-spin coupling and the spin-independent constant term by comparing Eq(23) and Eq(8). The RG calculation procedure can then be carried through as in the $\epsilon_1 = 0$ case described above.

4. Results for O/W(110)

We employed the method introduced in Section 3 to calculate the order-disorder transition temperature for several sets of $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$ values used in the Monte Carlo calculations of E.D. Williams et al.[2] The results are shown in table 1. Columns 1, 2, and 3 list the interaction energies arranged according to the ratio $-\epsilon_4/\epsilon_2$, which is given in Column 4. Column 5 gives the order-disorder transition temperature T_c obtained by Williams et.al.[2] using the Monte-Carlo method. Column 6 gives the value of T_c for $\epsilon_1 = 0$ in the free fermion approximation of Fan and Wu.[9] Our results are shown in Column 7 where the effect of ϵ_1 is neglected and column 8 where the effect of ϵ_1 is included as described

in Section 3. The ratios $T_c(\epsilon_1=0)/T_c(MC)$ and $T_c(\epsilon_1\neq 0)/T_c(MC)$ are shown in Columns 9 and 10, respectively. From table 1 we find that for $-\epsilon_4/\epsilon_2 \lesssim 0.7$ the difference between $T_c(\epsilon_1=0)$ and T_c(MC) is always less than 8% and for $-\epsilon_4/\epsilon_2 \lesssim 0.4$ the difference between $T(\epsilon_1\neq 0)$ and T_c (MC) is always less than 10%. Thus our method quite accurately predicts the transition temperature at half coverage for a certain range of $-\epsilon_4/\epsilon_2$. This range is close to physical reality because ϵ_4 is a longer distance interaction than ϵ_2 and thus will be weaker in general. It is also clear from Table I that while our approximate handling of ϵ_1 increases the error in T_c somewhat, the major part of it is due to the underlying treatment of the next nearest neighbor Ising model.

We have also calculated the average internal energy and specific heat of the system for the set of data ϵ_1 = -2.0 KCal/mole, $\epsilon_2 = \epsilon_3$ = 1.74 K cal/mole and ϵ_4 = -0.9 K cal/mole without taking the effect of last term in Eq(7) into account. The results are shown in Fig. 4. Comparing Fig. 4 with Fig. 7 of ref.(2), which was obtained by Monte-Carlo method, it is easy to see that our internal energy is very close to that obtained by the Monte-Carlo method. However the percentage difference between our specific heat and that obtained by the Monte-Carlo method is relatively large for temperatures far from T_c. Our specific heat is larger than that obtained by the Monte Carlo method for $T > T_c$ and smaller for $T < T_c$.

5. Critical Properties

The critical properties of the O/W(110) system are of considerable interest. This is because an argument based on the symmetry of the (2x1) ordered state[11] puts the order-disorder transition in the universality class of the XY model with cubic anisotropy and the eight vertex model[12]. This latter model, for which an exact solution exists, exhibits continuously varying critical order. That is, the transition is characterized by

critical exponents that vary continuously as a function of certain interaction parameters. In a renormalization group analysis, the mechanism for this involves a line of fixed points.

Now for O/W(110) there has been no measurement of critical properties to date. Further, the argument[11] that they should be in the eight vertex universality class is based on the symmetry of the ordered state only, and involved some assumptions that have not been completely justified. So the question of the critical properties of this system, or Eq(1), is of considerable interest.

We present several facts that indicate that the order-disorder transition of Eq(1) is Ising-like at one half coverage. This would mean that this coverage corresponds to the decoupling point[13] (four spin coupling K = 0) of the eight vertex model. Assuming the group theoretic arguments mapping O/W(110) onto the eight vertex model are correct, this would imply that the exponents along the rest of the order-disorder phase boundary vary continuously away from the Ising values. (Note especially that T_c at $\theta = 1/4$ is <u>not</u> independent[2] of ϵ_1).

First we note, in Eq(1), that if $\epsilon_1 = 0$ the model reduces to a simple antiferromagnetic Ising model with next-nearest neighbor interactions (on each sublattice). Such a model has not been solved exactly, but there is considerable evidence that it is in the universality class of the simple Ising model. Now as pointed out previously, Monte Carlo results[2] show that the transition temperature at one-half coverage, $T_c^{1/2}$, is independent of ϵ_1 over a considerable range of values. We have shown above that this remains true even if one considers $\epsilon_1 = 0$ (see Table I), at least within expected error. White it is <u>possible</u> for ϵ_1 to affect the critical exponents without changing $T_c^{1/2}$, it is quite unlikely, since this would require a line of fixed points parallel to the ϵ_1 ~~aix~~ axis over a very large region. The eight vertex fixed line is such that T_c depends on the "distance"

from the decoupling point. This picture is also consistent with the demonstration, in Section 2, that the ϵ_1 term is irrelevant at the $\epsilon_1 = 0$ fixed point.

A second bit of evidence is that we are able to get good results for $T_c^{1/2}$ with a renormalization group treatment that has only one (Ising-like) fixed point. Note that we do include ϵ_1 in our calculation, but its only effect is to renormalize the other coupling constants.

Finally, we recall the argument of Williams et.al.[2] mentioned in section 2. Consider a perfectly ordered (2x1) state (at $\theta = \frac{1}{2}$). Moving an adatom to the most favorable disordered site raises its energy by $\Delta\epsilon = 2\epsilon_2 + \epsilon_3 - \epsilon_4$ or $\Delta\epsilon = 2\epsilon_3 + \epsilon_2 - \epsilon_4$, depending on the orientation of the ordered state. This $\Delta\epsilon$ is independent of ϵ_1, which is again consistent with the independence of $T_c^{1/2}$ and an Ising type transition since this model is Ising like for $\epsilon_1 = 0$.

Now consider a spin representation[13] of the eight vertex model. In the perfectly ordered state, the two-spin excitation that preserves the number of up spins and has smallest $\Delta\epsilon$ in general involves both sublattices. However when the four-spin coupling K = 0, this is no longer true. Then one can ~~continue~~ confine the excitation to a single sublattice of the model, which has simple Ising coupling.

6. Future Research

It is clear from the results reported here that the renormalization group technique is a useful method for extracting AA interaction values from experimental surface phase diagrams with reasonable accuracy. To complete this program, however, it is necessary to generalize the method to coverages $\theta \neq \frac{1}{2}$. We have done some preliminary work and find reasonably good agreement for T_c at $\theta = \frac{1}{2}$ for the AA interaction parameters $\epsilon_1 = -2.64$, $\epsilon_2 = \epsilon_3 = 1.74$, $\epsilon_4 = -0.7$ kcal/mole. However it is clear that an accurate treatment for $\theta \neq \frac{1}{2}$ requires

generalizing the RG transformation in Eq(19) to include a term $\rho_0 \sum_1^4 \mu_i$ in the exponent, i.e. an effective magnetic field (or staggered field) acting on the transformed spin variables. Finding values of ~~po~~ ρ_0 and p that give accurate results will require some further study.

Acknowledgements

We are indebted to M. den Nijs for the application of the Kadanoff-Wegner argument presented in Section 2. The Monte Carlo values for T_c listed in Table I were kindly provided by Dr. E. Williams.

Figure Captions

Fig. 1. Absorption sites and adatom-adatom interactions ϵ_i for O/W(110). Both • and x denote adsorption sites. The former comprise the R sublattice and the latter the R' sublattice.

Fig. 2. Location of four spins on a typical R cell of the lattice.

Fig. 3. Spin couplings for the first bracket of Eq(21).

Fig. 4. Internal energy E and specific heat C_v for $\epsilon_1 = -2.0$,[9] $\epsilon_2 = \epsilon_3 = 1.74$ and $\epsilon_4 = -0.9$ kcal/mole calculated by the MKVM method.

Table Caption

Table I. Columns 1,2,3: adatom-adatom interaction energies

Column 4: $-\epsilon_4/\epsilon_2$

Column 5: transition temperature T_c as determined by Monte Carlo calculation[2].

Column 6: T_c from the free-fermion approximation[9] (for the ϵ_1=0 case).

Columns 8 and 9: T_c from the present work with ϵ_1=0 or $\epsilon_1 \neq 0$, respectively

Columns 9 and 10: ratios of the present values of T_c to the Monte Carlo results[2].

References

1. See T.L. Einstein, CRC Crit. Rev. Solid State Mater. Sic. 7, 261 (1978).

2. E. Williams, S. Cunningham, and W.H. Weinberg, J. Chem. Phys. 68, 4688 (1978).

3. W.Y. Ching et al, Surface Sci. 77, 550 (1978).

4. D.A. King, J. Vac. Sci. Technol. 17, 241 (1980).

5. G.-C. Wang, T.-L. Lu and M.G. Lagally, Phys. Rev. Letters 411 (1977); J. Chem. Phys. 69, 479 (1978).

6. Y.-M. Shih et al, Phys. Rev. B 21, 299 (1980).

7. A similar calculation for traingular lattices using the Migdal method has been reported by S. Ostlund and A.N. Berker, Phys. Rev. B 21, 5410 (1980).

8. L.P. Kadanoff and F.J. Wegner, Phys. Rev. B 4, 3689 (1971).

9. C. Fan and F.Y. Wu, Phys. Rev. 179, 560 (1969).

10. D.P. Landau, Phys. Rev. B 21, 1285 (1980).

11. See M.N. Barber, Phys. Reports 59, 375 (1980) and references therein.

12. R.J. Baxter, Phys. Rev. Letters 26, 832 (1971).

13. See ref. 8 (and ref. 4 therein).

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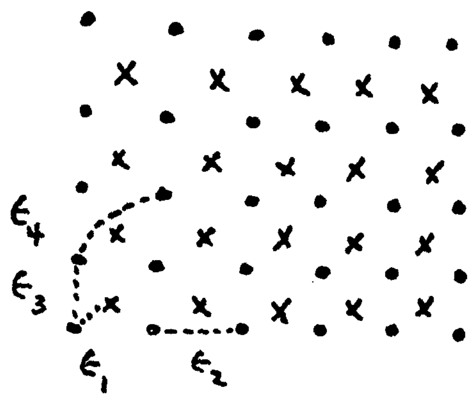


Fig 1

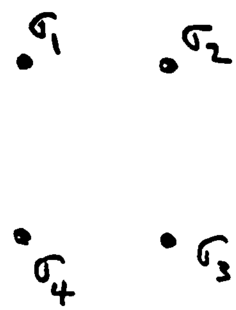
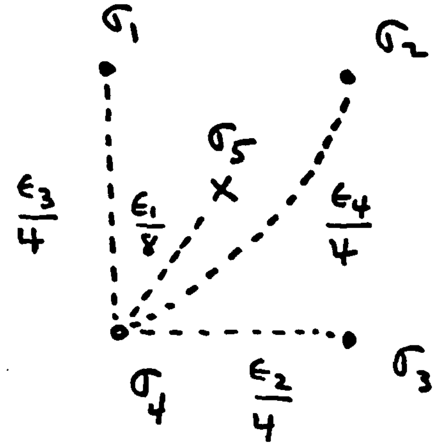


Fig 2



σ_1
σ_2
σ_5
$\frac{\epsilon_3}{4}$
$\frac{\epsilon_1}{8}$
$\frac{\epsilon_4}{4}$
σ_4
$\frac{\epsilon_2}{4}$
σ_3

Fig 3

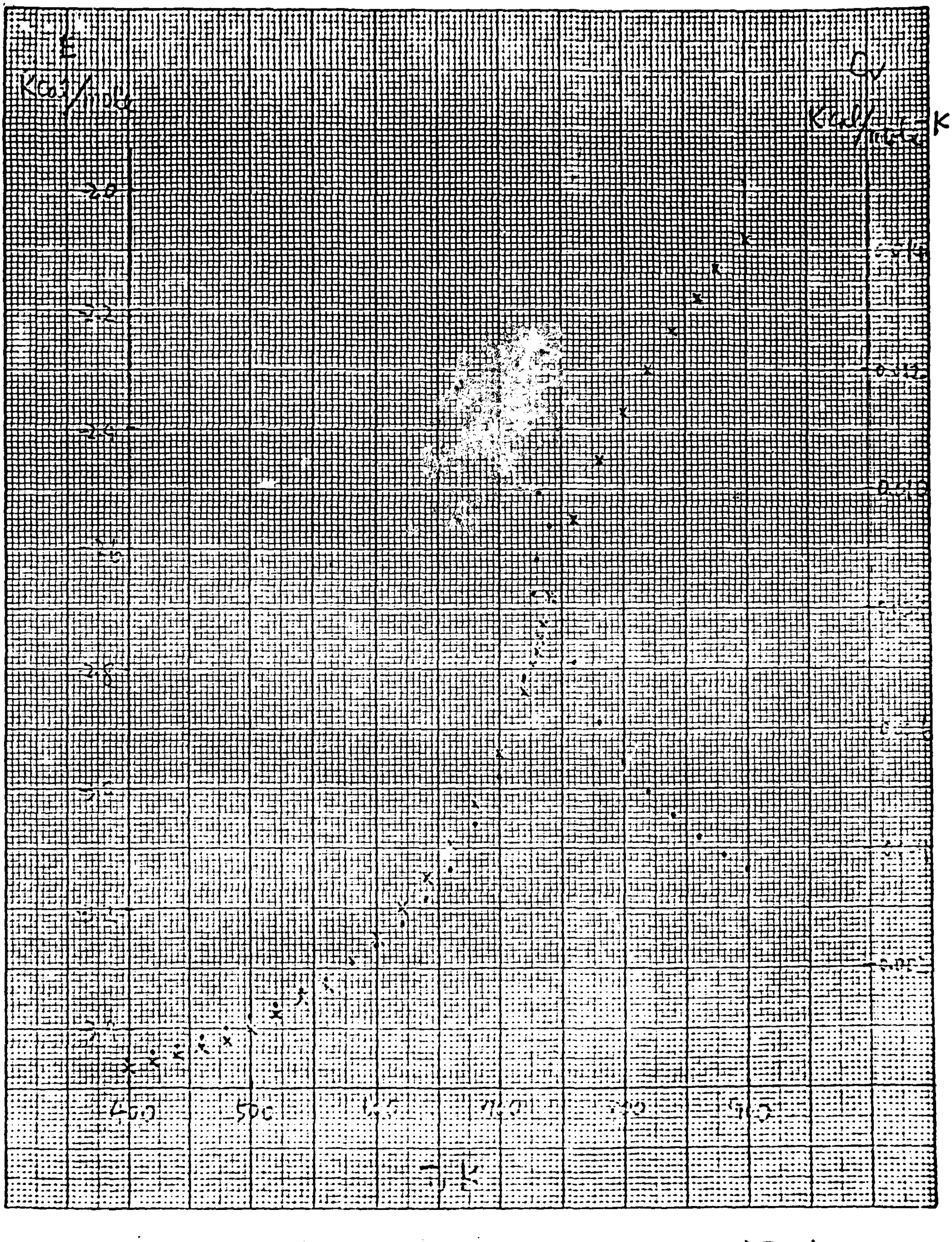


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Fig 4

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